Two photon polymerization lithography for 3D micro fabrication of single wall carbon nanotube/polymer composites

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ABSTRACT

Two photon polymerization (TPP) lithography has been established as a powerful tool to develop 3D fine structures of polymer materials[1,2], opening up a wide range applications such as micro-electromechanical systems (MEMS)[3]. TPP lithography is also promising for 3D micro fabrication of nanocomposites embedded with nanomaterials such as metal nanoparticles[4]. Here, we make use of TPP lithography to fabricate 3D micro structural single wall carbon nanotube (SWCNT)/polymer composites. SWCNTs exhibit remarkable mechanical, electrical, thermal and optical properties, which leads to enhance performances of polymers by loading SWCNTs. SWCNTs were uniformly dispersed in an acrylate UV-curable monomer including a few amounts of photo-initiator and photo-sensitizer. A femtosecond pulsed laser emitting at 780 nm was focused onto the resin, resulting in the photo-polymerization of a nanometric volume of the resin through TPP. By scanning the focus spot three dimensionally, arbitrary 3D structures were created. The spatial resolution of the fabrication was sub-micrometer, and SWCNTs were embedded in the sub-micro sized structures. The fabrication technique enables one to fabricate 3D micro structural SWCNT/polymer composites into desired shapes, and thus the technique should open up the further applications of SWCNT/polymer composites such as micro sized photomechanical actuators.

Keywords: 3D fabrication; Single wall carbon nanotube; Two photon polymerization; Lithography; Composites; Nanocomposites

1. INTRODUCTION

Optical lithography techniques have played a central role in nanotechnology, owing to the advantages for fabrication and integration of nanoscale components. In particular, two photon polymerization (TPP) lithography can develop 3D polymer structures with the feature resolution of sub-100 nm[5]. TPP lithography is based on photopolymerization stimulated by two photon absorption that occurs only in the vicinity of the focus spot of the excitation laser light. Therefore, TPP lithography allows to create arbitrary 3D fine polymer structures by scanning the focus spot three dimensionally. Since the first demonstration of TPP lithography was reported in 1997[1], TPP lithography has been widely applied in fields such as photonic devices[6], optical data storages[7], and MEMS[3]. Furthermore, TPP lithography is also promising for micro fabrication of nanocomposites embedded with nanomaterials. As an example, K. Masui et al. demonstrated micro fabrication of gold nanorods/polymer composites based on TPP lithography in 2011[4].

As filler materials in nanocomposites, single wall carbon nanotube (SWCNT) is one of the most attractive materials. SWCNTs are quasi-one dimensional carbon nanomaterials that consist of a rolled-up single layer graphene forming into hollow cylinder shape, of which the typical diameter and the length are ~1 nm and ~1000 nm, respectively. SWCNTs exhibit remarkable mechanical, electrical, thermal, and optical properties. Their Young's moduli and the strengths are ~1 TPa[8] and ~6 GPa[9], respectively, those are greater than other carbon fibers. Moreover, CNTs are highly conductive material due to ballistic transport resulting from their one-dimensional structure[10]. In addition, SWCNTs can be metallic or semiconducting depending on their chiralities, and the band gap of semiconducting-SWCNTs scales inversely with those diameter[11]. Their extremely high aspect ratio provides strong optical anisotropy[12]. These intrinsic properties as well as their unique one-dimensional structure make SWCNTs ideal candidates as advanced filler materials. Indeed, a great

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deal of efforts has been made for fabrication of SWCNT/composites to enhance mechanical[13], electrical[14], and thermal properties[15], and to add optical properties[16]. As another advantage of the use of SWCNTs as filler materials, their small size makes it possible to design micro- or even sub-micro-sized SWCNT/polymer composites. F. Ko et al. developed SWCNT/polymer composites in the form of nanowire with the diameter of 100 nm using electro-spinning method[17]. However, there have been no reports on 3D micro- or sub-micro fabrication of SWCNT/polymer composites as far as the authors' knowledge, probably because of lack of the spatial resolution of the conventional fabrication processing. There remains a huge challenge to achieve 3D micro/nano-fabrication of SWCNT/polymer composites.

Here, in order to solve the processing issue, we make use of TPP lithography for developing 3D micro structural SWCNT/polymer composites in the form of desired shapes. Our approach described here is to disperse SWCNTs into an UV-curable monomer and to fabricate micro/nano-structural SWCNT/polymer composites by using TPP lithography. This approach is expected to lead to further applications in fields such as micro sized photomechanical actuators.

2. Experimental

Figure 1(a) depicts a schematic preparation process of SWCNT-dispersed photo resin. SWCNTs, synthesized by the high-pressure carbon monoxide (HiPco) process at Rice University, were used in this study. SWCNTs were loaded into an acrylate monomer, R712[18], provided from Nippon Kayaku Co. Ltd. at a ratio of 0.01 wt%, and then dispersed by using an ultrasonic homogenizer (Branson Sonifier 250 Digital Ultrasonic Honogenizer). Photo-initiator (Benzil, Wako) and photo-sensitizer (2-benzyl- 2-(dimethylamino)-4'-morpholinobutyrophenon, Aldrich) were loaded into the compound at a ratio of 1.67 wt% and 1.67 wt%, respectively, and the resin was subsequently stirred for a few minutes. The two benzene rings in the monomer enable it to be stacked on the graphitic sidewalls of SWCNTs via π- π* interactions, which results in the stable dispersion of SWCNTs in the monomer (Fig.1 (b,c)). There were no macroscopic aggregations of SWCNTs in the photo resin, and SWCNTs were stably dispersed for more than a month.

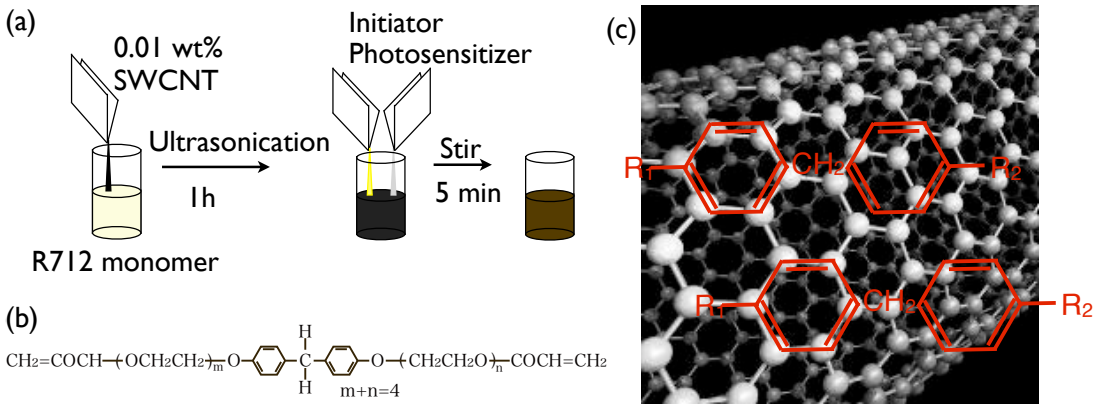

Figure 1. (a) Schematic preparation process of SWCNT-dispersed photo resin. (b) Chemical structure of an acrylate monomer, R712. (c) Schematic image of overlap of R712 monomer on SWCNT surface, resulting in the stable dispersion of SWCNTs.

Figure 2(a) shows an optical setup for 3D micro fabrication of SWCNT/polymer composites. A Ti:sapphire femtosecond pulsed laser (Tsunami, Spectra-Physics, Newport Corp.) emitting at 780 nm, with a pulse width and a repetition rate of 100 fs and 82 MHz, respectively, was used as a light source. The laser beam was tightly focused through an oil-immersion objective lens (100x, NA 1.4, Zeiss) onto the SWCNT-dispersed resin casted on a glass substrate placed on a three dimensional piezoelectric stage. The stage moved the resin relative to the focus spot according to preprogrammed patterns. The laser intensity was tuned to be ~15 GW/cm^2 by a neutral density filter. The exposure time was 4 ms at each scanning step controlled by a galvanometer shutter. By laser irradiation, solid polymer with CNTs embedded in it was created in the laser focus spot. After SWCNT/polymer composite structures were created, unsolidified resin was rinsed away using acetone, as illustrated in Fig. 2(b). The obtained structures were used for further characterization.

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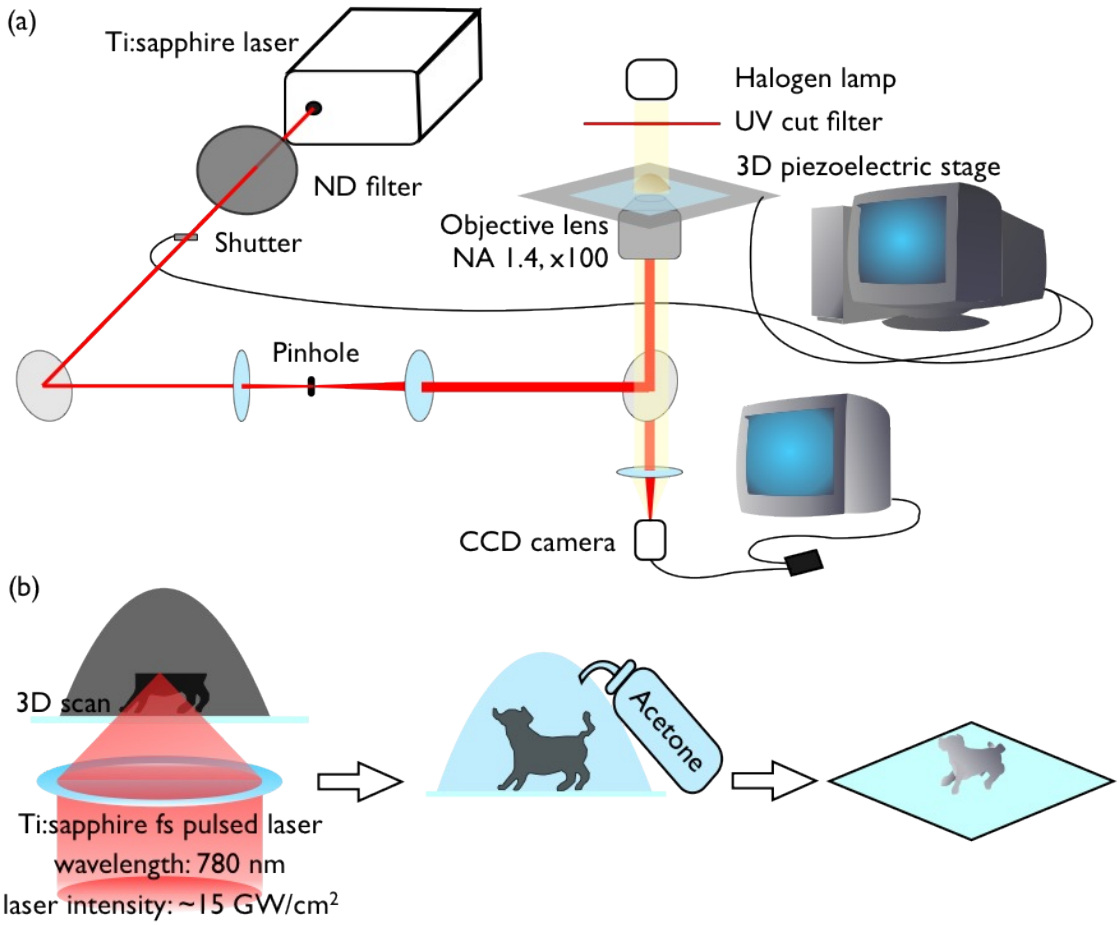

Figure 2. (a) Schematic of the optical setup for 3D micro fabrication of SWCNT/polymer composites. (b) Schematic developing process of micro structural SWCNT/polymer composites.

3. RESULTS & DISCUSSION

Figure 3 shows 3D micro/nano structural SWCNT/polymer composites fabricated by using TPP lithography. The scanning electron microscopic (SEM) images show that 3D micro/nano-structural SWCNT/polymer composites were fabricated based on programmed patterns, such as a micro-gear, a micro-logo, and character "CNT". The SEM images also indicate that the thickness of the thin part of the structure is smaller than 1 μm. This means that the spatial resolution of fabrication was sub-micrometer. These results consequently demonstrate that the fabrication technique exhibits the ability of 3D micro fabrication. Moreover, it is worth noticing that the surfaces of the structures are smooth, even though the widths of the structures are smaller than 1 μm like Fig.3 (d). This implies that SWCNTs are well dispersed in the photo resin. Otherwise, large aggregations (>1 μm) of SWCNTs could cause the distortion of the structural shapes during the developing process.

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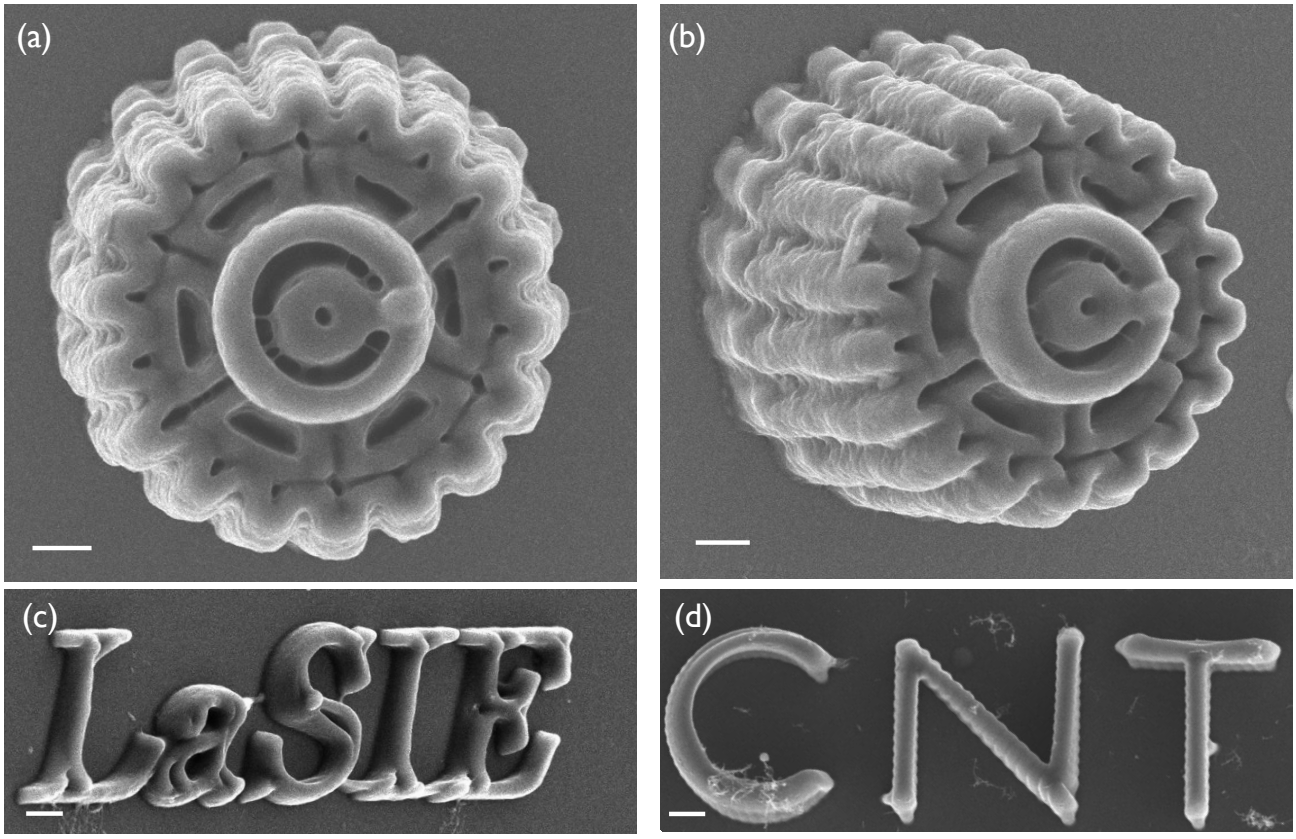

Figure 3 SEM images of 3D micro structural SWCNT/polymer composites fabricated by using TPP lithography. (a) Top view of a micro-gear. (b) Side view of the micro-gear. (c) a micro-logo of "LaSIE". (d) Character "CNT". All scale bars are 1 μm.

To investigate whether SWCNTs were surely embedded in the fabricated structures, we carried out Raman micro-spectroscopy. The Raman micro-spectroscopy experiments were conducted using a Raman microscope (Raman-11, Nanophoton Corp.) with an excitation wavelength of 785 nm and an objective lens (100x, NA 0.9, Nikon). The laser power and the exposure time were 2.2 mW and 30 s, respectively. The solid line in Fig.4 shows a Raman spectrum of the micro-structure "CNT". The measured area is indicated as a solid circle in the inset bright field image. The broken line in Fig.4 is a Raman spectrum taken beside the structure, namely in a dotted circle in the inset, as a reference. The Raman spectrum on the structure shows a pronounced peak at 1600 cm^{-1} that is assigned to tangential mode (G-band) arising from SWCNTs. On the other hand, there is no pronounced peak in the broken line. This result gives a clear indication that there were SWCNTs inside the fabricated polymer structures, even though the feature size of the structures is smaller than 1 μm. Consequently, the fabrication technique allows for embedding SWCNTs into the fine structures.

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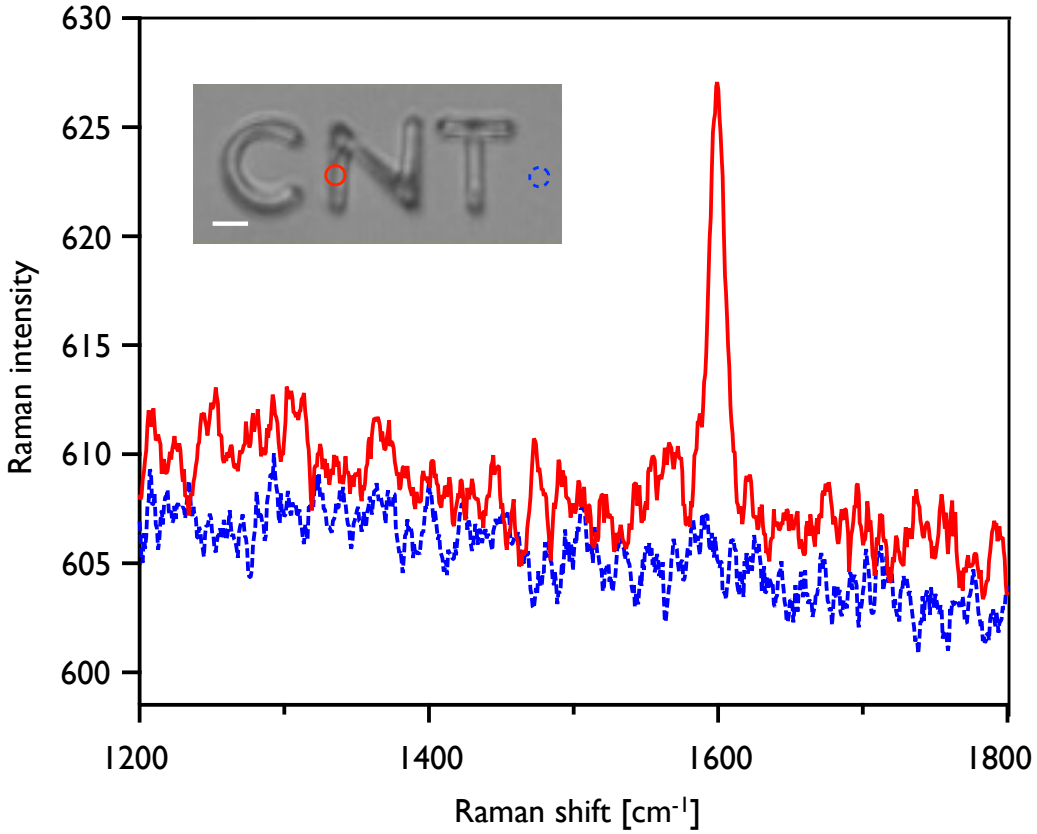

Figure 4 (Solid line) A Raman spectrum of the micro-structure "CNT". (Broken line) A Raman spectrum taken beside the structure. (Inset) A bright field image of the micro-structure "CNT". The solid and broken circles show the measured area of the Raman spectra of solid and broken line, respectively. The scale bar is 1 μm.

4. SUMMARY

We present a novel method for fabricating 3D micro structural single wall carbon nanotube (SWCNT)/polymer composites by using TPP lithography. SWCNTs were stably dispersed in an UV-curable resin without forming large aggregations, owing to π- π^* interactions between monomers and SWCNTs. TPP lithography was carried out on the SWCNT-dispersed photo resin, resulting in 3D micro fabrication of SWCNT/polymer composites in the form of desired shapes with the spatial resolution of sub-micrometer. Raman micro-spectroscopy experiment clearly showed that SWCNTs were embedded in the fabricated fine structures. The technique described here would be a significant progress on fabrication processing of SWCNT/polymer composites, promising for the further applications of SWCNT/polymer composites such as micro sized photomechanical actuators.

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